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(54) **Components for adhesive compositions and process for manufacture**

(57) Resins and oligomer materials and/or combinations thereof grafted with an unsaturated acid or anhydride, such as maleic anhydride, are disclosed herein. The grafted materials are useful in adhesive formulations, particularly in hot melt adhesive applications.

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Description

BACKGROUND

[0001] This invention relates to grafted hydrocarbon resins and oligomer compositions, including, but not limited to, adhesives and adhesive components incorporating the grafted compositions, and methods for making and using the compositions.

[0002] Relatively low molecular weight resins (usually with molecular weights ranging from 400 to 1500 Mn) are useful in many applications, including tackifying agents for adhesives, ink additives, polymer additives, road marking resins, paper sizing and pipe wrapping. Certain commercial grades of tall oil rosin esters (TOREs) or terpene phenolic resins (TPRs) are used to improve the performance of ethylene vinyl acetate (EVA)-based hot-melt adhesives (HMAs). TOREs, however, suffer from color instability and odor generation at application temperatures. Hydrocarbon resins, particularly hydrogenated cycloaliphatic resins, are superior in color stability and odor generation, but do not exhibit high all-around performance on polar surfaces, such as polyethylene terephthalate (PET) and acryclic varnishes, where TOREs are often used. The adhesive industry recognizes this problem but has yet to achieve a solution. Thus, a need exists for a hydrocarbon resin or an adhesive component having enhanced HMA performance without the instability and odor generation normally associated with TOREs or TPRs.

[0003] US Patent 4719260 discloses a hot-melt adhesive composition comprising an amorphous polymer containing polypropylene and a graft copolymer of a polycylic saturated aliphatic hydrocarbon resin and maleic anhydride having improved adhesion to substrates such as polyethylene. It does not disclose the use of an at least partially hydrogenated aromatic hydrocarbon resin. Further, it is generally known that aromatic resins are generally less compatible with saturated hydrocarbon polymers such as those described in US 4719260 and do not exhibit the same advantages in adhering to substrates such as polyethylene.

[0004] US 3161620 discloses a process for reacting maleic anhydride with thermally-produced hydrocarbon resins. It does not disclose at least partially hydrogenating the resin or oligomers before reaction with the maleic anhydride.

[0005] EP 0 088 510 discloses polar synthetic petroleum resins. In the embodiments disclosed therein the cyclopentadiene oligomer mixture is reacted with a carboxylic acid or anhydride such as phthalic or maleic acids and then hydrogenated. The reaction proceeds via the acid group reacting with the unsaturation of the resin oligomer thus forming an ester group at the point of attachment. The resulting resin product can be generally classified as a norbornyl ester. The grafted materials disclosed herein are believed to be produced through a different route, namely via an unsaturated bond of the acid or anhydride onto the resin which is preferably at least partially hydrogenated and more preferably substantially hydrogenated as defined herein.

[0006] Performance of hydrocarbon resins, particularly hydrogenated aromatic cycloaliphatic resins, on polar surfaces can be improved by modifying the resins to include polar functionality. Grafting functional components onto conventional hydrocarbon resins and/or resin oligomers and optionally combining the grafted resin or grafted oligomer material with another tackifying resin or other adhesive components improves performance and provides advantages over TOREs and TPRs when used in hot melt and other adhesive formulations. In particular, applicants have found that the adhesive materials incorporating these grafted components have improved compatibility with polar polymers such as EVA copolymers and exhibit good performance on difficult substrates, such as coated packaging surfaces.

SUMMARY

[0007] One embodiment disclosed herein is a composition comprising an at least partially hydrogenated material grafted with a graft monomer, wherein the material comprises: (a) a thermally-polymerized aromatic-containing hydrocarbon resin; or (b) an oligomer, in which case, the oligomer after it has been grafted with the graft monomer: (i) does not comprise norbornyl ester groups; or (ii) comprises at least one of a mono-alkyl succinic acid, anhydride or derivative thereof, or a β-alkyl substituted propanoic acid or derivative thereof; or, (c) a combination of (a) and (b). The composition may also comprise one or more reaction products of the material and the graft monomer or one or more products of the combination of the material and the graft monomer. The graft monomer is an unsaturated acid or anhydride or derivative thereof and has an olefinic bond through which it is grafted to the material, preferably an α, β olefinic bond. The graft monomer is preferably maleic anhydride. The material before grafting: (i) preferably contains less than 50% olefinic protons, more preferably less than 10% olefinic protons, and even more preferably less than 1% olefinic protons; and, (ii) preferably comprises aromatic monomers which are also present after hydrogenation and grafting.

[0008] The grafted material may be combined with at least one polyolefin to form an adhesive component. Suitable polyolefins include polyethylene, an ethylene α-olefin (C_3-C_{20}) copolymer, polypropylene, a propylene α-olefin (C_4-C_{20}) copolymer, polybutylene, a butylene α-olefin (C_5-C_{20}) copolymer, a polyisobutylene polymer or copolymer, block copolymers comprising styrene and one or more conjugated dienes, such as isoprene or butadiene, α-olefin diene copolymers, and mixtures of two or more thereof. The grafted material is typically well-suited for use with polar polymers,

including polyesters, polyamides, polyureas, polycarbonates, polyacrylonitriles, polyacrylates, polymethylacrylates, ethylene vinyl acetate copolymers, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate, polyacetals, ethylmethyl acrylate, ethylbutyl acrylate, and mixtures of two or more thereof.

[0009] Another embodiment disclosed herein is a process for making the above-mentioned composition(s). The process comprises contacting a graft monomer with an at least partially hydrogenated material comprising (a) a thermally polymerized aromatic-containing hydrocarbon resin; or (b) an oligomer, in which case, the oligomer after it has been grafted with the graft monomer: (i) does not comprise norbornyl ester groups; or (ii) comprises at least one of a mono-alkyl succinic acid, anhydride or derivative thereof, or a β-alkyl substituted propanoic acid or derivative thereof; or, (c) a combination of (a) and (b). The reaction preferably occurs in the presence of a free radical initiator. The product grafted material can be combined with other resins to form adhesive components and/or combined with one or more polyolefins as previously mentioned and further blended as needed and used as an adhesive.

DESCRIPTION OF THE FIGURES

[0010] Figures 1-6 illustrate the comparative performance on polyethylene and PET substrates between hot melt adhesives containing grafted resins and hot melt adhesives containing other resin materials.

[0011] Figures 7-12 illustrate the comparative performance on polyethylene and PET substrates between hot melt adhesives containing resin material comprising grafted oligomers and hot melt adhesives containing other resin materials.

[0012] Figures 13-15 illustrate the comparative performance on acrylic-coated oriented polypropylene film coated cardboard substrates between hot melt adhesives containing resin material comprising grafted oligomers and hot melt adhesives containing other resin materials.

DETAILED DESCRIPTION

Grafted Hydrocarbon Resin

[0013] As used herein, a grafted hydrocarbon resin, oligomer, and/or resin material, or a combination thereof means it has been combined, contacted, and/or reacted with a graft monomer. Grafting is the process of combining, contacting, or reacting the hydrocarbon resin, oligomers and/or resin material with the graft monomer. Grafting hydrocarbon resins, oligomer, and/or resin material, or a combination thereof to include at least some polar functionality produces useful components for many applications such as adhesive formulations, especially HMA formulations. These formulations are often designed for use with polar polymers, such as EVAs, ethylmethyl acrylates (EMAs), polyacrylates (PAs), polymethacrylates (PMAs), ethylene alkyl acrylates and for use on polar substrates, such as PET, recycled paper, cardboard, and acrylic varnishes and work well on other substrates such as wood, glass, ceramic, asphalt, concrete, and metal.

[0014] Accordingly, embodiments of the present invention include grafted and ungrafted hydrocarbon resin(s) and oligomer(s) and combinations and mixtures thereof. Embodiments also include, but are not limited to: adhesives or adhesive components comprising (i) grafted hydrocarbon resins; (ii) grafted oligomers, (iii) grafted oligomers + ungrafted resin(s), (iv) grafted hydrocarbon resin + ungrafted resin(s), (v) grafted hydrocarbon resin + ungrafted oligomers, (vi) grafted hydrocarbon resin + grafted oligomers, (vii) grafted oligomers + ungrafted oligomers or (viii) grafted hydrocarbon resin + grafted oligomers + ungrafted resin(s) and other suitable combinations of one or more thereof. The embodiments described herein also include processes for making and using the previously described materials.

[0015] Suitable hydrocarbon resins that may be grafted include: aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, and mixtures of two or more thereof. Rosin esters may also be grafted. Preferably, the resin is at least partially hydrogenated and comprises aromatic monomers. In one embodiment, the weight ratio of graft monomer:resin in a grafted resin product is preferably between 1:1000 and 1:1, more preferably between 1:100 and 1:1, more preferably between 1:50 and 1:1, more preferably between 1:10 and 1:1, more preferably between 1:3 and 1:1, and even more preferably between 1:100 and 3:10.

[0016] In one embodiment, the resin comprises hydrocarbon resins produced by the thermal polymerization of cyclopentadiene (CPD) or substituted CPD, which may further include aliphatic or aromatic monomers as described later. In one embodiment, the hydrocarbon resin has an aromatic content of 1-60 %, more preferably 1-40 %, more preferably 1-20 %, more preferably 10-20 %, more preferably 15-20 %, more preferably 1-10 %, and more preferably 5-10 %.

[0017] As used herein aromatic content and olefin content are measured by ^{1}H-NMR as measured directly from

the ^1H NMR spectrum from a spectrometer with a field strength greater than 300 MHz, most preferably 400 MHz (frequency equivalent). Aromatic content is the integration of aromatic protons versus the total number of protons. Olefin proton or olefinic proton content is the integration of olefinic protons versus the total number of protons.

[0018] In another embodiment, the resin is preferably at least partially hydrogenated and more preferably substantially hydrogenated. As used herein at least partially hydrogenated means that the material contains less than 90% olefinic protons, more preferably less than 75 % olefinic protons, more preferably less than 50 % olefinic protons, more preferably less than 40 % olefinic protons, more preferably less than 25 % olefinic protons, more preferably less than 15 % olefinic protons, more preferably less than 10 % olefinic protons, more preferably less than 9 % olefinic protons, more preferably less than 8 % olefinic protons, more preferably less than 7 % olefinic protons, and more preferably less than 6 % olefinic protons. As used herein, substantially hydrogenated means that the material contains less than 5% olefinic protons, more preferably less than 4 % olefinic protons, more preferably less than 3 % olefinic protons, more preferably less than 2 % olefinic protons, more preferably less than 1 % olefinic protons, more preferably less than 0.5 % olefinic protons, more preferably less than 0.1% olefinic protons, and more preferably less than 0.05% olefinic protons. The degree of hydrogenation is typically conducted so as to minimize and preferably avoid hydrogenation of the aromatic bonds.

[0019] In one embodiment, the hydrocarbon resin to be grafted has a softening point of 10-200°C, more preferably 10-160°C, more preferably 60-130°C, more preferably 90-130°C, more preferably 80-120°C, more preferably 80-150°C, and more preferably 90-110°C and is preferably at least partially hydrogenated. Softening point (°C) is preferably measured as a ring and ball softening point according to ASTM E-28 (Revision 1996).

Grafted oligomers

[0020] Another embodiment is a material comprising grafted oligomers (dimers, trimers, tetramers, pentamers, and hexamers), preferably derived from a petroleum distillate boiling in the range of 30-210°C. The oligomers can be derived from any suitable process and are often derived as a byproduct of resin polymerization. Suitable oligomer streams have molecular weights (Mn) between 130-500, more preferably between 130-410, more preferably between 130-350, more preferably between 130-270, more preferably between 200-350, and more preferably between 200-320. Examples of suitable oligomer streams include, but are not limited to, oligomers of cyclopentadiene and substituted cyclopentadiene, oligomers of C_4-C_6 conjugated diolefins, oligomers of C_8-C_{10} aromatic olefins, and combinations thereof. Other monomers may be present. These include C_4-C_6 mono-olefins and terpenes. The oligomers preferably comprise one or more aromatic monomers and are at least partially hydrogenated, more preferably substantially hydrogenated. In one embodiment, the grafted oligomer material has an oligomer:graft monomer molar ratio between 50:1 and 1:2, more preferably between 10:1 and 2:1, more preferably between 5:1 and 2:1, more preferably between 1.5:1 and 1:1.5, and more preferably about 1:1.

[0021] As stated, both the resins and oligomers preferably comprise one or more aromatic monomers. The data below suggests that an aromatic material yields better performance in adhesives comprising aromatic-containing graft material. Additionally, certain graft monomers, such as maleic anhydride, have good solubility in an aromatic-containing material which probably allows for a more homogeneous reaction phase and likely avoids undesirable byproducts during the grafting reaction.

Graft Monomers

[0022] Preferred graft monomers include any unsaturated organic compound containing at least one olefinic bond and at least one polar group such as a carbonyl group, which includes unsaturated acids and anhydrides and derivatives thereof. Preferably, the organic compound contains an ethylenic unsaturation conjugated with a carbonyl group (-C=O) and preferably contains at least one α, β olefin bond. Examples include carboxylic acids, acid halides or anhydrides, phenols, alcohols, ethers, ketones, alkyl and aromatic amines, nitriles, imines, isocyanates, nitrogen compounds, halides and combinations and derivatives thereof. Representative acids and acid derivatives include carboxylic acids, anhydrides, acid halides, esters, amides, imides and their salts, both metallic and non-metallic. Examples include maleic, fumaric, acrylic, methacrylic, itaconic, aconitic, citraconic, himic, tetrahydrophthalic, crotonic, α-methyl crotonic, and cinnamic acids. Maleic anhydride is a particularly preferred graft monomer. Particular examples include, itaconic anhydride, citraconic anhydride, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, glycidyl acrylate, monoethyl maleate, diethyl maleate, dibutyl maleate, monomethyl fumarate, dimethyl fumarate, monomethyl itaconate, diethyl itaconate, acrylamide, methacrylamide, maleic acid monoamide, maleic acid diamide, maleic acid-N-monoethylamide, maleic acid-N,N-diethylamide, maleic acid-N-monobutylamide, maleic acid-N,N-dibutylamide, fumaric acid monoamide, fumaric acid diamide, fumaric acid-N-monobutylamide, fumaric acid-N,N-dibutylamide, maleimide, N-butylmaleimide, N-phenylmaleimide, sodium acrylate, sodium methacrylate, potassium acrylate and potassium methacrylate.

Hydrocarbon Resin Production

[0023] Hydrocarbon resins are well known and are produced, for example, by Friedel-Crafts polymerisation of various feeds, which may be pure monomer feeds or refinery streams containing mixtures of various unsaturated materials. Generally speaking, the purer the feed the easier to polymerise. For example pure styrene, pure α-methyl styrene and mixtures thereof are easier to polymerise than a C_8/C_9 refinery stream. Similarly, pure or concentrated piperylene is easier to polymerise than C_4-C_6 refinery streams. These pure monomers are, however, more expensive to produce than the refinery streams which are often by-products of large volume refinery processes.

[0024] Aliphatic hydrocarbon resins can be prepared by cationic polymerisation of a cracked petroleum feed containing C_4, C_5, and C_6 paraffins, olefins, and conjugated diolefins commonly referred to as C_5 monomers. These monomer streams comprise cationically polymerisable monomers such as butadiene, 1,3-pentadiene (piperylene) along with cyclopentene, pentene, 2-methyl-2-butene, 2-methyl-2-pentene, isoprene, cyclopentadiene, and dicyclopentadiene. To obtain these feeds the refinery streams are purified usually by both fractionation and treatment to remove impurities.

[0025] The resin polymerization feed may also comprise aromatic monomers such as styrene, indene, derivatives of styrene, derivatives of indene, and combinations thereof. Particularly preferred aromatic olefins include styrene, α-methylstyrene, β-methylstyrene, indene, methylindenes and vinyl toluenes.

[0026] In addition to the reactive components, non-polymerisable components in the feed may include saturated hydrocarbons such as pentane, cyclopentane, or 2-methyl pentane that can be co-distilled with the unsaturated components. This monomer feed can be co-polymerised with other C_4 or C_5 olefins or dimers. Preferably, however, the feeds are purified to remove unsaturated materials that adversely affect the polymerisation reaction or cause undesirable colours in the final resin (e.g., isoprene). This is generally accomplished by fractionation. In one embodiment, polymerization is conducted using Friedel-Crafts polymerisation catalysts such as supported or unsupported Lewis acids (e.g., boron trifluoride (BF_3), complexes of boron trifluoride, aluminium trichloride ($AlCl_3$), complexes of aluminium trichloride or alkyl aluminium halides, particularly chlorides).

[0027] Typically, the feed stream includes between 20-80 wt% monomers and 20-80 wt% solvent. Preferably, the feed stream includes 30-70 wt% monomers and 30-70 wt% of solvent. More preferably, the feed stream includes 50-70 wt% monomers and 30-50 wt% of solvent. The solvent may include an aromatic solvent, which may be toluenes, xylenes, other aromatic solvents, aliphatic solvents and/or mixtures of two or more thereof. The solvent is preferably recycled. The solvent may comprise the unpolymerisable component of the feed. The solvents generally contain less than 250 ppm water, preferably less than 100 ppm water, and most preferably less than 50 ppm water.

[0028] The feed stream may include at least some C_4-C_6 monomers, wherein cyclopentadiene and methylcyclopentadiene components are optionally removed from the feed stream by heating it to a temperature between 100°C and 160°C and fractionating by distillation. The monomers may include at least one member selected form the group consisting of isobutylene, butadiene, 2-methyl-2-butene, 1-pentene, 2-methyl-1-pentene, 2-methyl-2-pentene, 2-pentene, cyclopentene, isoprene, cyclohexene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,3-hexadiene, 1,4-hexadiene, cyclopentadiene, and dicyclopentadiene.

[0029] In another embodiment, the feed stream includes 30-95 wt% of C_5 monomers, as described above and 5-70 wt% of a co-feed including at least one member selected from the group consisting of pure monomer, C_9 monomers, and terpenes. Preferably, the feed stream includes about 50-85 wt% of C_5 monomers and about 15-50 wt% of a co-feed, including at least one member selected from the group consisting of pure monomer, C_9 monomers, and terpenes.

[0030] Typically, the resulting hydrocarbon resin has a number average molecular weight (Mn) of 400-3000, a weight average molecular weight (Mw) of 500-6000, a z-average molecular weight (Mz) of 700-15,000 and a polydispersity (PD) as measured by Mw/Mn between 1.5 and 4. As used herein, molecular weights (number average molecular weight (Mn), weight average molecular weight (Mw),and z-average molecular weight (Mz)) are measured by Size Exclusion Chromatography using a Waters 150 Gel Permeation Chromatograph equipped with a differential refractive index detector and calibrated using polystyrene standards. Samples are run in tetrahydrofuran (THF) (45°C). Molecular weights are reported as polystyrene-equivalent molecular weights and are generally measured in g/mol.

[0031] The monomer feed can be co-polymerised with C_4 or C_5 olefins or their olefinic dimers as chain transfer agents. Up to 40 wt%, preferably up to 20 wt%, of chain transfer agents may be added to obtain resins with lower and narrower molecular weight distributions than can be prepared from using the monomer feed alone. Chain transfer agents stop the propagation of a growing polymer chain by terminating the chain in a way, which regenerates a polymer initiation site. Components, which behave as chain transfer agents in these reactions include but are not limited to, 2-methyl-1-butene, 2-methyl-2-butene or dimers or oligomers of these species. The chain transfer agent can be added to the reaction in pure form or diluted in a solvent.

[0032] In one embodiment, the resin is preferably obtained by thermal polymerisation of a feed comprising unsaturated monomers of cyclopentadiene and/or substituted cyclopentadiene. In one embodiment, the feed also comprises aromatic monomers as previously described. In such embodiments, a mixture of (a) a steam cracked petroleum distillate

boiling in the range 80-200°C containing about dimers and codimers of cyclopentadiene and its methyl derivatives together with (b) a steam cracked distillate boiling in the range 150-200°C comprising α-methyl styrene, vinyl toluenes, indene and methyl indene with other C_9 and C_{10} aromatics, in the weight ratio (a:b) between 90:10 to 50:50 is heated in a batch polymerization reactor to 160-320°C at a pressure of 9.8×10^5-11.7×10^5 Pa for 1.5 to 4 hrs. Where inclusion of the oligomers is not desired, the resulting polymerizate may steam stripped to remove inert, unreacted, and low molecular weight oligomeric components to yield a resin having a softening point in the range 80-120°C.

[0033] The products of the polymerization process include both resin and an oligomer by-product comprising oligomers (dimers, trimers, tetramers, pentamers, and hexamers) of the feed monomer(s). As used hereafter, resin material refers to the resin, the oligomers, or a mixture of the two. In an embodiment where the oligomer by-product results from thermal polymerization of CPD and substituted CPD, the oligomers are typically a complex mixture of (preferably hydrogenated as described below) Diels Alder trimers and tetramers of CPD and methyl-CPD with low levels of acyclic C_5 diolefins such as pentadiene-1,3 and isoprene.

[0034] The resin material is then preferably hydrogenated to reduce coloration and improve colour stability. Any of the known processes for catalytically hydrogenating resin material can be used. In particular the processes disclosed in US 5171793, US 4629766, US 5502104 and US 4328090 and WO 95/12623 are suitable. Generic hydrogenation treating conditions include reactions in the temperature range of about 100-350°C and pressures of between five atmospheres (506 kPa) and 300 atm (30390 kPa) hydrogen, for example, 10-275 atm (1013-27579 kPa). In one embodiment the temperature is in the range including 180-330°C and the pressure is in the range including 15195-20260 kPa hydrogen. The hydrogen to feed volume ratio to the reactor under standard conditions (25°C, 1 atm (101 kPa) pressure) typically can range from 20:1-200:1; for water-white resins 100:1-200:1 is preferred. The hydrogenated product may be stripped to remove low molecular weight by-products and any solvent. This oligomeric by-product is a low-viscosity nearly colorless liquid boiling between 250-400°C and is preferably substantially hydrogenated.

[0035] The hydrogenation of the resin material may be carried out via molten or solution based processes by either a batch wise or, more commonly, a continuous process. Catalysts employed for the hydrogenation of hydrocarbon resins are typically supported monometallic and bimetallic catalyst systems based on group 6, 8, 9, 10 or 11 elements. Catalysts such as nickel on a support (for example, nickel on alumina, nickel on charcoal, nickel on silica, nickel on kieselguhr, etc), palladium on a support (for example, palladium on silica, palladium on charcoal, palladium on magnesium oxide, etc) and copper and/or zinc on a support (for example copper chromite on copper and/or manganese oxide, copper and zinc on alumina, etc) are good hydrogenation catalysts. The support material is typically comprised of such porous inorganic refractory oxides as silica, magnesia, silica-magnesia, zirconia, silica-zirconia, titania, silica-titania, alumina, silica-alumina, alumina-silicate, etc, with supports containing γ-alumina being highly preferred. Preferably, the supports are essentially free of crystalline molecular sieve materials. Mixtures of the foregoing oxides are also contemplated, especially when prepared as homogeneously as possible. Useful support materials include those disclosed in the US Patent Nos. 4686030, 4846961, 4500424, and 4849093. Suitable supports include alumina, silica, carbon, MgO, TiO_2, ZrO_2, FeO_3 or mixtures thereof.

[0036] Another suitable process for hydrogenating the resin material is described in EP 0082726. EP 0082726 describes a process for the catalytic or thermal hydrogenation using a nickel-tungsten catalyst on a gamma-alumina support wherein the hydrogen pressure is 1.47×10^7 - 1.96×10^7 Pa and the temperature is in the range of 250-330°C. After hydrogenation the reactor mixture may be flashed and further separated to recover hydrogenated resin material. In one embodiment, steam distillation may be used to separate the oligomers and is preferably conducted without exceeding 325°C resin temperature.

[0037] In one embodiment, the catalyst comprises nickel and/or cobalt on one or more of molybdenum, tungsten, alumina or silica supports wherein the amount of nickel oxide and/or cobalt oxide on the support ranges from 2-10 wt%. The amount of tungsten or molybdenum oxide on the support after preparation ranges from 5-25 wt%. Preferably, the catalyst contains 4-7 wt% nickel oxide and 18-22 wt% tungsten oxide. This process and suitable catalysts are described in greater detail in US Patent 5820749. In another embodiment, the hydrogenation may be carried out using the process and catalysts described in US Patent 4629766. In particular, nickel-tungsten catalysts on gamma-alumina are preferred.

[0038] In one embodiment, the oligomers are stripped from the resin before hydrogenation. In such an embodiment, the oligomers are preferably hydrogenated before grafting. In another embodiment, the oligomers are hydrogenated with the resin and then stripped from the resin, yielding a hydrogenated resin and hydrogenated oligomers. In another embodiment, at least some of the oligomers are stripped before hydrogenation and at least some hydrogenated oligomers are stripped after hydrogenation. In yet another embodiment, the hydrogenated resin/oligomers product may be further processed together as a single mixture as described below. In yet another embodiment, the oligomers can be derived from any suitable source and hydrogenated (if necessary) before grafting so that the oligomers before grafting are typically at least partially hydrogenated and preferably susbstantially hydrogenated.

Grafting the Resin Material

[0039] At least a portion of the resulting resin material, preferably derived from a process such as that described above, may then be combined and/or contacted with a graft monomer, typically under suitable reaction conditions and in a suitable mixing device. In accordance with the previously described embodiments, the resin and oligomers may be grafted separately or simultaneously, and if separately, grafted oligomers may then be optionally remixed with the grafted resin, an ungrafted resin, or any another suitable resin, adhesive component or composition as described below.

[0040] Grafting of the graft monomer preferably occurs in the presence of a free-radical initiator selected from the group consisting of organic peroxides, organic peresters, and azo compounds. Examples of such compounds include benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(peroxybenzoate)hexyne-3, 1,4-bis(tert-butylperoxyisopropyl)benzene, lauroyl peroxide, tert-butyl peracetate, 2,5-dimethyl-2,5-di (tert-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butyl perbenzoate, tert-butylperphenyl acetate, tert-butyl perisobutyrate, tert-butyl per-sec-octoate, tert-butyl perpivalate, cumyl perpivalate and tert-butyl perdiethylacetate, azoisobutyronitrile, dimethyl azoisobutyrate. The peroxide preferably has a half-life of about 6 minutes at 160°C with volatile non-aromatic decomposition products and those that minimize color formation. Preferred peroxides include di-tert-butyl peroxide and 2,5 dimethyl-2,3-di(tert-butylperoxy)hexane. The amount of peroxide combined is typically dependent on the weight of the graft monomer. In one embodiment, the weight ratio of the graft monomer: peroxide in the reaction mixture may be between 1:1 and 20:1, more preferably between about 1:1 and 10:1, more preferably between about 1:1 and about 5:1 and even more preferably about 4:1.

[0041] The graft monomers may be combined with the resin material at a temperature between 50-200°C, more preferably between 70-150°C, more preferably between 70-125°C, more preferably between 140-180°C, more preferably between 140-180°C, more preferably between 155-165°C or between 165-175°C and a pressure of typically one atmosphere but higher pressures can be used if necessary. The graft monomer may be combined so that the weight ratio of graft monomer:resin material is less than 1:1, more preferably less than 5:10 more preferably less than 3:10 and more preferably less than 3:20. In a preferred embodiment, the reaction mixture is maintained in a homogenous state. The reaction mixture is preferably agitated or stirred vigorously. The free radical initiator is combined with the resin material-graft monomer reaction mixture either in one addition or preferably in a continuous or semi continuous mode during the reaction. Residence time in the reaction zone is preferably less than 75 minutes, more preferably less than 60 minutes, even more preferably between 30-60 minutes.

[0042] In embodiments where only the oligomers are grafted, the reaction temperature is preferably between 50-200°C, more preferably between 70-150°C, more preferably between 70-125°C, more preferably between 140-180°C, more preferably between 140-180°C, more preferably between 155-165°C, and more preferably about 160°C. The amount of graft monomer added is typically dependent on the amount of oligomer. Preferably, the oligomer: graft monomer mole ratio is between 5:1 and 1:5, more preferably between 2:1 and 1:2, more preferably between about 1.5:1 and 1:1.5 and more preferably about 1:1. Thereafter, the ungrafted oligomers are stripped from the product and optionally recycled to the reaction zone. The grafted oligomers produced generally have a softening point between 0-120°C, more preferably between 25-120°C, more preferably between 50-120°C and even more preferably between 80-110°C and color of 4-10 Gardner. Gardner color, as used herein, is measured using ASTM D-6166. The grafted oligomer product can then be recombined with the resin (grafted or ungrafted) from which it was derived or combined with other resins, polymers, and/or other materials and formulated into and adhesive material.

[0043] In embodiments where only the resin is grafted, the reaction temperature is preferably between 50-200°C, more preferably between 70-150°C, more preferably between 70-125°C, more preferably between 140-180°C, more preferably between 140-180°C, more preferably between 165-175°C, and more preferably about 170°C. The amount of graft monomer added is typically dependent on the amount of resin. The graft monomer:resin weight ratio in the reaction mixture is preferably less than 1:5, more preferably less than 1:10, more preferably less than 1:20, and even more preferably about 1:40. Generally, the grafting raises the softening point of the resin less than 10°C, more preferably less than 5°C and produces a grafted resin having a color between 2-6 Gardner.

[0044] In another embodiment, the oligomers are not stripped from the resin product, and the resin and oligomers are simultaneously grafted. Reaction conditions are similar to those previously described for grafting the resin, but the graft monomer:resin material weight ratio is generally kept below 1:2, more preferably below 5:20 and more preferably below 3:20. Upon completion of grafting, the material may be further stripped if required to yield a resin of the desired softening point and/or to remove unreacted oligomers. Separation of the grafted oligomers from the grafted resin may also be made if desired, but the product may be used without such further processing. In many emobodiments comprising grafted resin and grafted oligomers, the weight ratio of grafted oligomers:grafted resin in the resin material will be greater than 1:200, more preferably greater than 1:100, more preferably greater than 1:50, more preferably greater than 1:20, and more preferably greater than 1:10.

[0045] Grafting of the resin material can also be conducted via a solution route wherein the resin material dispersed in a solvent and combined, contacted and/or reacted with the graft monomer. Additionally or alternatively, the graft

monomer can be dispersed in a solvent prior to adding to the resin material. These routes allow for lower reaction temperatures (as low as 100°C) and allows the choice of different peroxides having half-lives of 6 minutes at the lower reaction temperatures. Suitable solvents include, but are not limited to, alipahtic solvents, cycloaliphatic solvents, aromatic solvents, and aromatic-aliphatic solvents. Typical examples include benzene, toluene, xylene, chlorobenzene, n-pentane, n-hexane, n-heptane, n-octane, n-decane, iso-heptane, iso-decane, iso-octane, cyclohexane, alkyl cyclohexane, and combinations of two or more thereof.

[0046] It is believed that the graft monomer is grafted to the resin material through an olefinic bond of the graft monomer such as an α, β olefinic bond. It is believed that by grafting the oligomers via this route, the formation of norbornyl ester groups in the grafted resin material is minimized and preferably avoided. The resulting grafted oligomers are preferably at least one of a (i) a mono-alkyl succinic acid, anhydride or derivative thereof, or (ii) a β-alkyl substituted propanoic acid or derivative thereof. The reaction product of the resin material and graft monomer or the product of the combination of the resin material and the graft monomer may also include some oligomers of the graft monomer, which may or may not be removed before formulating a final composition.

[0047] The resulting grafted resin material preferably has a softening point between 15-210°C, more preferably 15-170°C, more preferably 65-140°C, more preferably 65-130°C, more preferably 80-120°C, more preferably 90-110°C, and more preferably between about 85-110°C. The grafted resin material preferably has a glass transition temperature (Tg) less than 120°C, more preferably less than 110°C, more preferably less between 25-100°C, more preferably between 60-100°C, more preferably 60-80°C, and more preferably between 35-70°C. Differential Scanning Calorimetry (DSC, ASTM D 34188-88) was used to measure Tg.

Blending with Other Resins

[0048] Any previously described embodiment of the resin material may be blended with another tackifying resin. Suitable examples of other tackifying resins include: aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic/aromatic hydrocarbon resins, aromatic hydrocarbon resins, at least partially hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosin esters, resins grafted with graft monomers, and mixtures of any two or more thereof. Suitable resins also include other resins having polar functionality whether produced by processes described herein or other suitable processes.

[0049] For example, one embodiment is a composition comprising between 0.1-99 wt% grafted resin material and between 1-99.9 wt% other resin. Other embodiments comprise between 0.1-50 wt% grafted resin material, between 0.1-30 wt% grafted resin material, between 0.1-20 wt% grafted resin material, between 1-25 grafted resin material, between 1-15 wt% grafted resin material, between 1-10 wt% grafted resin material, between 5-10 wt% grafted resin material, and between 10-30 wt% grafted material.

[0050] In a preferred embodiment, the resin material comprises grafted resin and grafted oligomers in embodiments of between 0.1 and 50 wt% grafted oligomers, more preferably between 0.1 and 30 wt% grafted oligomers, more preferably between 0.1 and 20 wt% grafted oligomer, more preferably 0.1 and 10 wt% grafted oligomers, more preferably between 1 and 30 wt% grafted oligomers more preferably between 1 and 20 wt% grafted oligomers, and more preferably between 1 and 10 wt% grafted oligomers based on the total weight of the resin material.

Blending into Adhesive Components and Compositions

[0051] Any of the previously described embodiments may be combined with other adhesive components and formulated into pressure sensitive adhesives, HMAs, or contact adhesives used in applications such as tapes, labels, paper impregnation. HMA applications include woodworking, packaging, bookbinding or disposables. The embodiments described herein can also be formulated into compositions for sealants, rubber compounds, pipe wrapping, carpet backing, contact adhesives, road-marking and/or tires. These compositions may be used without further dilution as in the case of HMAs or they may be diluted in appropriate solvents to form solvent-based adhesives (SBAs) or dispersed in water to form resin emulsions for water-borne adhesives (WBAs).

[0052] Any of the previously described embodiments may be combined with or formulated into adhesives comprising polar polymers. As used herein, polar polymers include homopolymers, copolymers, and terpolymers containing polar groups such as esters, ethers, ketones, amides, imides, alcohols, phenols, halides, acids, anhydrides, sulphides, nitriles, isocyanates, aromatic and heteroaromatic groups. These polar substituents may be found in the polymer backbone, pendant to the polymer backbone or attached to an aromatic group that may be either incorporated in the polymer backbone or pendant to the polymer backbone. Suitable examples include copolymers of a C_2 to C_{20} olefin, such as ethylene and/or propylene and/or butene with one or more polar monomers such as vinyl esters or alcohols, acids,

anhydrides, acrylic or methacrylic acids or esters. Polar polymers also include any thermoplastic copolymer comprising a functional group capable of interacting with the unsaturated acid or anhydride group present with the resin material. Examples include, but are not limited to, polymers (or copolymers of) such as polyesters, polyamides, polyureas, polycarbonates, polyacrylonitriles, polyacrylates, polymethylacrylates, ethylene vinyl esters, halogenated polymers, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate (PBT), polyacetal, acrylic or methacrylic acids, alkyl acrylates, or methacrylates and the like. Accordingly, in one embodiment, the grafted resin material may be formulated with a polar polymer, such as EVA. It may optionally comprise other components such as one or more waxes or oils.

[0053] Any of the previously described embodiments may be combined or combined with a polyolefin (base polymer) to form an adhesive. Typical base polymers include polyethylene, ethylene copolymerized with one or more C_3 to C_{20} linear, branched, or cyclic α-olefins, polypropylene, propylene copolymerized with one or more of ethylene and/ or C_4 to C_{20} linear, branched, or cyclic α-olefins, polybutylene, polybutylene copolymerized with one or more of C_5 to C_{20} linear, branched, or cyclic α-olefins, low density polyethylene (LDPE) (density 0.915 to less than 0.935 g/cm^3) linear low density polyethylene (LLPDE), ultra low density polyethylene (density 0.86 to less than 0.90 g/cm^3), very low density polyethylene (density 0.90 to less than 0.915 g/cm^3), medium density polyethylene (density 0.935 to less than 0.945 g/cm^3), high density polyethylene (HDPE) (density 0.945 to 0.98 g/cm^3). Other hydrocarbon polymers (or copolymers of) include: polybutene-1, polyisobutylene, polybutene, polyisoprene, polybutadiene, butyl rubber, amorphous polypropylene, ethylene propylene diene monomer rubber, natural rubber, styrene butadiene rubber, copolymers and halogenated copolymers of isobutylene and para-alkylstyrene, elastomers such as ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymers of styrene and one or more conjugated dienes such as SI (Styrene-Isoprene), SBS (Styrene-Butadiene-Styrene), SB (Styrene-Butadiene), SIS (Styrene-Isoprene-Styrene), nylons, polycarbonates, PET resins, polymers of aromatic monomers such as polystyrene, copolymers of isobutylene and para-alkyl styrene, high molecular weight HDPE, low molecular weight HDPE, graft copolymers generally, polyacrylonitrile homopolymer or copolymers, thermoplastic polyamides, polyacetal, polyvinylidine fluoride and other fluorinated elastomers, polyethylene glycols, polyisobutylene, or blends thereof. Preferred α-olefins include propylene, butene, pentene, hexene, heptene, octene, nonene, dodecene, cyclopentene, 3,5,5-trimethylhexene-1, 3-methylpentene-1, 4-methyl pentene-1 and terpolymers of the above monomers. In another embodiment, the copolymer comprises a terpolymer of (i) ethylene and/or (ii) a C_3 to C_{20} comonomer, and (iii) a diene. Preferred dienes include butadiene, pentadiene, hexadiene, norbornene, ethylidene norbornene, vinylidene norbornene, dicyclopentadiene, and substituted versions thereof. The architecture of such polymers may be linear, substantially linear, short-chain branched, long-chain branched, star branched or any other combination thereof. The branches or arms may be the same as the main backbone or different such as branch-block polymers or multi-armed stars.

[0054] Any of the previously described embodiments may be blended with grafted polymers or blends of grafted polymers and/or non-grafted polymers. Examples of polymers and of such blends include, but are not limited to, those described in US 5,936,058.

[0055] Any of the previously described embodiments may be blended with elastomers to form adhesive sealants. Preferred elastomers include natural rubber, polyisoprene, polybutadiene, copolymers of butadiene with styrene, copolymers of butadiene with acrylonitrile, butyl rubber, polychloroprene, ethylene/propylene rubber and elastomeric copolymers of ethylene, propylene and a non-conjugated diene, styrenic block copolymers such as block copolymers of styrene and or α-methyl styrene with an alkadiene (such as isoprene or butadiene) in linear, radial, and/or tapered form.

[0056] In one embodiment, the base polymer may be a polymer produced using a metallocene catalyst system. Typically, the metallocene homopolymers or copolymers are produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion in solution, slurry, high-pressure or gas phase. The catalyst system may be supported or unsupported and the cyclopentadienyl rings may be substituted or unsubstituted. Titanium, zirconium and hafnium are preferred transition metals. Several commercial products produced with such catalyst/activator combinations are commercially available from ExxonMobil Chemical Company in Baytown, Texas under the tradenames EXCEED® and EXACT® or from Dow Chemical Company under the tradenames ENGAGE® and AFFINITY®.

[0057] The metallocene produced copolymers described above preferably have a polydispersity less than 4 and a composition distribution breadth index (CDBI) of 50 % or more, preferably above 60%, even more preferably above 70%. In one embodiment, the CDBI is above 80%, even more preferably above 90%, even more preferably above 95%. In one embodiment, the polyethylene copolymer has a CDBI between 60-85%, even more preferably between 65-85%.

[0058] Composition Distribution Breadth Index (CDBI) is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published February 18, 1993 including that fractions having a weight average molecular weight (Mw) below 15000 are ignored when determining CDBI.

[0059] Any of the previously described embodiments may be present in a blend of resin and base polymer. Suitable ratios of resin:base polymer include 1:1000 to 2:1, more preferably 1:2 to 2:1 and even more preferably between 3:1 and 1:3.

[0060] Any of the previously described embodiments may be admixed with additives well known in the art such as processing oils, performance oils, anti-block, anti-static, antioxidants, cross-linking agents, silica, carbon black, talc, pigments, fillers, processing aids, UV stabilizers, neutralizers, lubricants, anti-slip agents, slip agents, surfactants and/or nucleating agents. Examples of common additives include: antioxidants such as Irganox® 1010, silicon dioxide, titanium dioxide, polydimethylsiloxane, talc, dyes, wax, calcium stearate, carbon black and glass beads. In HMA applications, suitable synthetic waxes include paraffin and microcrystalline waxes having melting points within a range from about 55°C to about 130°C and low molecular weight polyethylene and Fischer-Tropsch waxes. The wax content is preferably from about 1 to about 35 wt.% of the total blend composition. In PSA applications, suitable oils include FLEXON® 876 or PRIMOL® 352 available from ExxonMobil Chemical Company at concentrations less than 50%.

[0061] Any of the previously described embodiments may be formulated into pressure sensitive adhesives that may be applied to any conventional backing layer such as paper, foil, polymeric film, release liners, woven or non-woven backing material to make for example, packaging tapes, masking tapes and labels.

[0062] Optional components in an HMA embodiment are plasticizers or other additives such as oils, tackifiers, surfactants, fillers, color masterbatches, and the like. Preferred plasticizers include mineral oils, polybutenes, phthalates, and the like. Particularly preferred plasticizers include phthalates such as diisodecyl phthalate (DIOP), diisononylphthalate (DINP), dioctylphthalates (DOP). Particularly preferred oils include aliphatic naphthenic oils.

[0063] Another optional component of an HMA composition is a low molecular weight product such as wax, oil, or low Mn polymer, (low meaning below Mn of 5000, preferably below 4000, more preferably below 3000, even more preferably below 2500). Preferred oils include aliphatic naphthenic oils, white oils, or the like. Preferred low Mn polymers include polymers of lower α olefins such as propylene, butene, pentene, and hexene. A particularly preferred polymer includes polybutene having a Mn of less than 1000. An example of such a polymer is available under the trade name PARAPOL™ 950 from ExxonMobil Chemical Company. PAAAPOL™ 950 is a liquid polybutene polymer having a Mn of 950 and a kinematic viscosity of 220cSt at 100 °C, as measured by ASTM D 445.

[0064] HMAs embodiments can be used for disposable diaper and napkin chassis construction, elastic attachment in disposable goods converting, packaging, labeling, bookbinding, woodworking, and other assembly applications. Particular examples include: baby diaper leg elastic, diaper frontal tape, diaper standing leg cuff, diaper chassis construction, diaper core stabilization, diaper liquid transfer layer, diaper outer cover lamination, diaper elastic cuff lamination, feminine napkin core stabilization, feminine napkins adhesive strip, industrial filtration bonding, industrial filter material lamination, filter mask lamination, surgical gown lamination, surgical drape lamination, and perishable products packaging.

Additives for Polymers

[0065] The embodiments of this invention have novel utility as polymer additives in many applications. Other materials may be present depending upon the application. Many of the classes of polymer have been described earlier in the text. They may be used in polymer processing, for example in various molding applications where good spiral flow is needed and retention of physical properties is needed. A wide range of polymers, from polypropylene to engineering thermoplastics, are in this category. The resins of this invention also aid adhesion, cling, and tack. A wide range of polymers, for example in polyolefin films, tyre rubber compositions or rubber overmolded articles, are in this category. They may also be added to ink formulations to aid adhesion of the components as well as to the substrates. Other applications are in paint drying and concrete curing.

Additives for Road Marking

[0066] The embodiments disclosed herein may be formulated into thermoplastic road-marking (TRM) compositions. Such formulation comprises a resin, plasticizer or an oil, pigment, fillers, glass beads. The grafted material of the invention can be used as the primary resin of the road-marking composition or as an additional additive to the road-marking composition. The road-marking compositions containing the grafted material of the invention can additionally comprise EVA, polyisobutylene, block copolymers comprising sytrene and a conjugated diene such as isoprene or butadiene (including, but not limited to SI, SIS, SB, and/or SBS), polyethylene waxes, rosin esters, rosin derivatives, maleic acid/anhydride modified hydrocarbon resin. The grafted material of the invention aids the dispersion of fillers and pigment yielding improved properties of fluidity and color.

Cross-linking and Reactive Processing

[0067] The embodiments of this invention have a further advantage as polymer additives in inks and construction and road marking applications. They are capable of creating and participating in cross-linking within the composition medium by cross-linking with the other components of the adhesive formulation. The preferable example of anhydride or acid groups on the resin can cross-link with themselves or with other polymers present in the composition medium. Some polymers containing amine or alcoholic functionality will react directly with the grafted resin material, e.g., those polymers containing some vinyl alcohol groups. Others polymers will cross-link when a cross-linking agent is added. In these embodiment, the amount of cross-linking agent added is typically dependent on the amount of graft monomer present. Typical amounts include between 100:1 and 1:100, more preferably 1:1 parts cross linking agent per parts graft monomer (molar ratio) present in the formulation. These include polymers containing some acrylic acid such as ethylene alkyl-acrylate acrylic acid terpolymers or polymers containing succinic anhydride or acid groups such as maleic anhydride grafted ethylene propylene diene rubbers. Such cross-linking can be achieved in many ways, including the addition of difunctional agents capable of reacting with the acid or anhydride groups. Examples of such materials are those containing alcohol and amine functionality such as diols, diamines, especially primary amines. The material having these functional groups may be mixed or have different substitutions, for example a diamine where one group is primary and the other is tertiary. Weaker cross-linking can be achieved via interactions which do not form covalent bonds such as ionic and hydrogen bonds. Examples of materials capable of cross-linking in such a manner are divalent metal ions such as Ca^{++} or diamines containing quaternary amines.

Examples

[0068] In the following examples HMAs were prepared as follows. The components of the HMA formulation was introduced in a Z-blade mixer previously heated at 180°C under nitrogen blanketing. The waxes were introduced after 10 minutes, and the mixing was continued for another 60 min. The mixer was stopped, the nitrogen blanket was stopped, and the blend was poured into a tray. The blend was further cooled under nitrogen blanket and covered with a release paper.

[0069] HMA specimens were prepared for testing as follows. The adhesive was introduced in the hopper of an accumeter and molted at 150°C under nitrogen. Strips of desired substrate carriers (polyethylene film of 200µ thickness, PET film of 100µ thickness, aluminium of 90µ thickness and/or acrylic-coated oriented polypropylene (OPP) film cardboard) were cut and coated with the molten adhesive.

[0070] For T-Peel testing, the HMA specimens were prepared for testing by cutting coated and un-coated substrates into pieces of about 25 cm length and 10 cm width. The non-coated substrate was laid on top of the coated substrate. The specimen was wrapped into a release paper which was further laminated with a hot press at a given temperature depending on the substrate, (110°C for polyethylene, acrylic-coated OPP cardboard, 150°C for Al, polypropylene and polyethylene terephthalate (PET)) under a pressure of 4400 pounds (114 psi/783 kPa) for 30 seconds. Strips of 2 cm width were cut from the laminated specimen(s) with a paper cutter in the coating direction. T-Peel strengths were measured with a tensile tester (Zwick). The F-average force (g/cm) for peeling was measured (average of at least 3 test specimens for each laminate). When jerking was indicated, 2/3 of the maximum peak was recorded. Failure types were also recorded in Tables 1-5: Adhesive Failure (AF), Cohesive Failure (CF), Jerking or No Jerking, and Tear.

[0071] Shear Adhesion Failure Temperature (SAFT) and Hot Shear test specimens were prepared the same as for T-Peel specimens except that strips of 25 x 70 mm were used and laid on stainless steel plates previously cleaned.

[0072] SAFT was determined by adhering a coated strip of the selected substrate to stainless steel with a contact area of 12.5 x 25 mm, hanging the samples in an oven held at 25°C and suspending a 500 g weight from the bottom of the strip. The temperature was raised at 0.4°C/min and the bond failure temperature was measured. The Shear Adhesion Failure Temperature was the average of three tests.

[0073] Hot shear was measured by suspending a 1000 gram weight from a 25 mm wide strip of the selected substrate coated with the adhesive formulation which was adhered to a stainless steel plate with a contact area of 12.5 x 25 mm. The sample was placed in a ventilated oven at 40°C. Time was recorded until stress failure occurs. Typically, these tests were made and recorded individually to determine reliability of the holding power.

[0074] Saponification number was measured according to the following procedure. 2g of powdered resin material was dissolved in 25ml toluene/isopropanol (1:1 wt ratio) and 50ml of 0.1N alcoholic KOH was added by pipette. After refluxing for 30 min and cooling to room temperature the solution was titrated against 0.1N HCl using phenolphthaleine indicator. A blank run was carried out without resin material. Saponification number (mg KOH/g resin) was then calculated by multiplying 56.1 (approximate molecular weight of KOH) x volume of standard HCl x Normality of HCl divided by the weight of resin material sample.

[0075] In the following examples, all parts, proportions, and percentages are by weight unless otherwise indicated.

Example 1

[0076] A thermally polymerized hydrogenated aromatic containing CPD resin (available as Escorez®5600 from ExxonMobil Chemical Europe having a softening point of 103°C, Mn 270, and Tg 55°C) was blended in an HMA formulation consisting of 45 parts resin, 35 parts EVA (Escorene® 40028 available from ExxonMobil Chemical Company), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant (Irganox® 1010 available from CIBA-GEIGY). T-Peel on polyethylene to polyethylene and PET to PET, and Hot Shear and SAFT on polyethylene to stainless steel and on PET to stainless steel were measured. The results from Example 1 are shown in the Tables and are used as a reference for comparison with later examples.

Example 2

[0077] A tall oil rosin ester available as Sylvalite RE 100 available from Arizona Chemical Company (softening point 96°C, Mn 950, Mw 1110) was blended in an HMA formulation consisting of 45 parts rosin ester, 35 parts EVA (Escorene® 40028), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant (Irganox® 1010). T-Peel on polyethylene to polyethylene, PET to PET and acrylic-coated OPP cardboard to acrylic-coated OPP cardboard, and Hot Shear and SAFT were measured on polyethylene to stainless steel, on PET to stainless steel, and on acrylic-coated OPP cardboard to stainless steel. The results from Example 2 are shown in the Tables and are used as a reference for comparison with later examples.

Example 3

[0078] A tall oil rosin ester available as Sylvalite RE 100 available from Arizona Chemical Company (softening point 100°C, Mn 810, Mw 1060) was blended in an HMA formulation consisting of 45 parts rosin ester, 35 parts EVA (Escorene® 40028), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant (Irganox® 1010). T-Peel on polyethylene to polyethylene and PET to PET, and Hot Shear and SAFT on polyethylene to stainless steel and on PET to stainless steel were measured. The results from Example 3 are shown in the Tables and are used as a reference for comparison with later examples.

Example 4

[0079] A terpene phenolic resin available as Dertophene T from Derives Resiniques Terpeniques (softening point 95°C, Mn 490, Mw 700, initial color 4.5 Gardner) was blended in an HMA formulation consisting of 45 parts terpene phenolic resin, 35 parts EVA (Escorene® 40028), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant (Irganox® 1010). T-Peel on polyethylene to polyethylene and PET to PET, and Hot Shear and SAFT on polyethylene to stainless steel and on PET to stainless steel were measured. The results from Example 4 are shown in the Tables and used as a reference for comparison with later examples.

Example 5

[0080] 100g of a thermally polymerized hydrogenated aromatic containing CPD resin, same as the Escorez® 5600 resin tested in Example 1, but without anti-oxidant, containing 7.5% aromatic protons and 0.01% olefinic protons having a softening point of 103°C, was heated to and maintained at 170°C in a 250 ml flask fitted with a stirrer under nitrogen. 5.5 g dibutyl maleate was added. Four aliquots of 0.75 ml 2,5-dimethy-2,5-di(tert-butylperoxy)hexane (Luperox® 101) were added at 15 minute intervals. After completion of the peroxide addition the mixture was stirred for a further 75 minutes under a nitrogen flow to remove volatile materials. The resulting reaction product was poured from the reactor, cooled and analysed. The grafted resin product had a Gardner colour of 3.5 (50 wt% in toluene), a softening point of 84°C, and a Saponification number of 17.

Example 6

[0081] 100g of a thermally polymerized partially hydrogenated aromatic containing CPD resin, same as the Escorez® 5600 resin tested in Example 1, but without anti-oxidant, having a softening point 103°C, 7.5% aromatic protons and 0.01% olefinic protons indicated by ^1H NMR spectroscopy was heated in a 500 ml flask fitted with stirrer under nitrogen to and maintained at 170°C. When liquid, 1.23g maleic anhydride powder was added and blended. Five 0.1 ml aliquots of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (Luperox 101) were added to the stirred liquid at 15 minute intervals and the reaction was continued for a further 60 minutes with a flow of nitrogen to remove volatile peroxide decomposition products and any residual unreacted maleic anhydride. The melt was poured out of the reaction flask and allowed to

cool and solidify. The resulting grafted resin had a softening point 105°C, Gardner colour of 3.5, and a Saponification number of 10.

Example 7

[0082] 250g of a thermally polymerized partially hydrogenated aromatic containing CPD resin, same as the Escorez® 5600 resin tested in Example 1, but without anti-oxidant, having a softening point 103°C and 7.5% aromatic and 0.01% olefinic protons as indicated by ^{1}H NMR spectroscopy was heated in a 500 ml flask fitted with stirrer under nitrogen to and maintained at 170°C. When liquid, 6.13g maleic anhydride powder was added and blended. Five 0.25 ml aliquots of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane were added to the stirred liquid at 10 minute intervals and the reaction was continued for a further 20 minutes with a flow of nitrogen to remove volatile peroxide decomposition products and any residual unreacted maleic anhydride. The melt was poured out of the reaction flask and allowed to cool and solidify. The resulting grafted resin had a softening point 105°C, Gardner colour of 3.6, and a Saponfication number of 20.

Example 8

[0083] 100g of a thermally polymerized partially hydrogenated aromatic containing CPD resin, same as the Escorez® 5600 resin tested in Example 1, but without anti-oxidant, having a softening point 103°C, 7.5% aromatic protons and 0.01% olefinic protons as indicated by ^{1}H NMR spectroscopy was heated in a 500 ml flask fitted with stirrer under nitrogen to and maintained at 170°C. When liquid, 4.9g maleic anhydride powder was added and blended. Four 0.5 ml aliquots of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane were added to the stirred liquid at 15 minute intervals and the reaction was continued for a further 75 minutes with a flow of nitrogen to remove volatile peroxide decomposition products and any residual unreacted maleic anhydride. The melt was poured out of the reaction flask and allowed to cool and solidify. The resulting grafted resin had a softening point 112°C, Gardner colour of 8, and a Saponfication number of 40.

Examples 9-12

[0084] The grafted resins from Examples 5-8 were blended in an HMA formulation was blended in an HMA formulation consisting of 45 parts grafted resin, 35 parts EVA (Escorene® 40028), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant (Irganox®1010). T-Peel on polyethylene to polyethylene and PET to PET, and Hot Shear and SAFT on polyethylene to stainless steel and on PET to stainless steel were measured. The results for Examples 9-12 are shown in Tables 1 and 2 and Figure 1-6. Note for T-Peel: only the peeling force (F-average) was represented. When the sample was only jerking, it corresponds to a zero adhesion force.

[0085] These results show that on polyethylene substrates, most of the grafted resins perform similarly to reference Examples 1-4 for adhesion. On the other hand, for Hot Shear and SAFT most of the grafted resins are superior to references Examples 1-4, especially examples 6/10, 7/11 and 8/12 where graft monomer was maleic anhydride. These results also illustrate that on a polar substrate such as PET, the grafted resins have better adhesion compared to the ungrafted resin of Example 1 and the tall oil rosin esters of Examples 2 and 3, which show only jerking. As illustrated in Figures 1-6, the Hot Shear and SAFT results show that the grafted resins of Examples 6/10, 7/11 and 8/12 are equal to or superior to the reference Examples 1-4.

Table 1

Grafted Resin HMA formulations

Polyethylene Substrates

Example(s)	1	2	3	4	5/9	6/10	7/11	8/12
Cloud Point (°C)	85	88	145	85	84	84	83	>200
Softening Point (°C)	101	105	104	103	102	102	102	103
T-Peel PE/PE (g/cm)	874	1098	720	1306	968	1045	1036	673
Failure Type	AF+CF	CF	AF	CF	CF	CF	CF	CF PE Tear
T-Peel PE/PE (g/cm)	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	CF
Hot Shear PE/ss (minutes at 60°C)	23	16	15	17	14	28	29	27
SAFT PE/ss (°C)	67	66	65	66	64	67	68	68

Table 2

Grafted Resin HMA formulations

Polyethylene Terephthalate Substrates

Example(s)	1	2	3	4	5/9	6/10	7/11	8/12
Cloud Point (°C)	85	88	145	85	84	84	83	>200
Softening Point (°C)	101	105	104	103	102	102	102	103
T-Peel PET/PET (g/cm)	0	0	0	293	546	0	0	225
Failure Type	Jerking	Jerking	Jerking	CF + Jerking	CF	Jerking	Jerking	CF
T-Peel PET/PET (g/cm)	15	287	228	509	454	154	225	252
Hot Shear PET/ss (minutes at 60°C)	25	<21	33	23	25	34	35	36
SAFT PET/ss (°C)	67	68	67	67	65	68	69	69

Example 13

[0086] 700g of a hydrogenated trimer and tetramer mixture of oligomers of cyclopentadiene, methyl cyclopentadiene and C_9-C_{10} aromatic olefins was removed from the overhead stream of a product stripping tower in a commercial manufacturing process for a thermally polymerized aromatic containing CPD hydrocarbon resin at an ExxonMobil production facility in Notre Dame de Gravenchon, France. The oligomers obtained did not contain anti-oxidant and contained 7.4 % aromatic protons and 0 % olefinic protons. The oligomers were stirred under nitrogen at 160°C with 70g maleic anhydride powder in a 2 liter flask. Six 3 ml aliquots of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane were added at 0, 10, 20, 30, 45 and 75 minutes elapsed time. The reaction stirring continued for a further 45 minutes with a flow of nitrogen through the flask to remove any volatile components. The reactor was cooled to 140°C and the product was poured into cold paraffinic hydrocarbon solvent having boiling in the range of 160-192°C by ASTM D-1078 (available as Exxsol D from ExxonMobil Chemical Europe). The insoluble reaction product was filtered off and washed with heptane to remove residual traces of unreacted oligomers and any peroxide decomposition products. The yield was 120 g of grafted oligomers having softening point 107°C, Gardner Color 12 (acetone:toluene 1:1 wt), and a Saponification number of 336.

Example 14-17

[0087] The grafted oligomers from Example 13 were blended with a thermally polymerized hydrogenated aromatic containing CPD resin (Escorez® 5600) in various ratios of oligomers to resin to form a resin material. The resin material was then blended in an HMA formulation consisting of 45 parts resin material, 35 parts EVA (Escorene® 40028), 10 parts polyethylene Np wax, 10 parts polyethylene FT wax and 0.5 parts anti-oxidant such as Irganox®-1010. T-Peel on polyethylene to polyethylene and PET to PET, and Hot Shear and SAFT on polyethylene to stainless steel and on PET to stainless steel have been measured. The amounts of grafted oligomer in the resin material was varied between 5 and 30 wt%. The results from Examples 14-17 are shown in Tables 3 and 4 and Figures 7-12. T-Peel tests on Examples 15 and 17 were also conducted on acrylic-coated OPP cardboard and compared to similar results generated with an HMA formulation produced by Example 2. Those results are shown in Table 5 and Figures 13-15.

[0088] Tables 3 and 4 and Figures 7-12 illustrate that resin materials containing grafted oligomers show overall comparable behavior on polyethylene substrates when compared to reference Examples 1-4. These results also illustrate that on a polar substrate such as PET, a significant advantage is achieved with resin material containing grafted oligomers, especially for adhesion. These results also illustrate that Hot Shear and SAFT are significantly higher for resin material containing grafted oligomers when compared to reference Examples 1-4. The results from Table 5 and Figures 13-15 also illustrate that the resin material containing grafted oligomers has superior performance over the tall oil rosin ester tested in Example 2 on acrylic-coated OPP cardboard, especially for adhesion.

[0089] As is apparent from the foregoing description, the materials prepared and the procedures followed relate to specific preferred embodiments of the broad invention. It is apparent from the foregoing general description and the specific embodiments that, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of this invention. Accordingly, it is not intended that the invention be limited thereby. In the following claims which represent the invention in specific embodiments, each dependent embodiment for each of the below independent embodiments may be practiced with one or more of the limitations of the other dependent embodiments so as to represent other operable embodiments within the scope of the invention claimed.

Table 3

Grafted Oligomer/Hydrocarbon Resin HMA formulations

Polyethylene Substrates

Example(s)	1	2	3	4	13/14	13/15	13/16	13/17
Cloud Point (°C)	85	88	145	85	>200	>200	>200	>200
Softening Point (°C)	101	105	104	103	102	102	102	103
Resin Material								
Grafted Oligomers (wt%)					5	10	20	30
Hydrocarbon resin (wt%)					95	90	80	70
T-Peel PE/PE (g/cm)	874	1098	720	1306	733	966	885	1018
Failure Type	AF+CF	CF	AF	CF	AF PE Tear	CF PE Tear	AF + CF PE Tear	AF + CF PE Tear
T-Peel PE/PE (g/cm)	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking	No Jerking
Hot Shear PE/ss (minutes at 60°C)	23	16	15	17	24	17	13	23
SAFT PE/ss (°C)	67	66	65	66	67	67	68	68

Table 4

Grafted Oligomer/Hydrocarbon Resin HMA formulations

Polyethylene Terephthalate Substrates

Example(s)	1	2	3	4	13/14	13/15	13/16	13/17
Cloud Point (°C)	85	88	145	85	>200	>200	>200	>200
Softening Point (°C)	101	105	104	103	102	102	102	103
T-Peel PET/PET (g/cm)	0	0	0	293	0	0	495	494
Failure Type	Jerking	Jerking	Jerking + AF	CF	Jerking	CF Tendency to Jerk	AF + CF	CF
T-Peel PET/PET (g/cm)	15	287	228	509	50	219	Tendency to Jerk	No Jerking
Hot Shear PET/ss (min. at 60°C)	23	16	15	17	44	174	108[1]	0
SAFT PET/ss (°C)	67	68	67	67	90[2]	109[3]	93[4]	50

Superscripts indicate average measurement, ranges disclosed as follows, [1]36-180, [2]69-110, [3]86->120, [4]75-110

Table 5

Grafted Oligomer/Hydrocarbon Resin HMA formulations Acrylic-Coated OPP on Cardboard Substrates			
Example(s)	2	13/15	13/17
Cloud Point (°C)	88	>200	>200
Softening Point (°C)	105	102	103
T-Peel AC / AC (g/cm)	0	294	507
Failure Type	Jerking	AF	AF
T-Peel AC/AC (g/cm)	274	No Jerking	No Jerking
Hot Shear AC/ss (minutes at 60°C)	102	126	152
SAFTPET/ss (°C)	100	107	>113

Claims

1. A composition comprising an at least partially hydrogenated material grafted with a graft monomer, wherein the material comprises:

(a) a thermally polymerized aromatic-containing hydrocarbon resin;
(b) an oligomer, in which case, the oligomer after it has been grafted with the graft monomer:

(i) does not comprise norbornyl ester groups; or
(ii) comprises at least one of a mono-alkyl succinic acid, anhydride or derivative thereof, or a β-alkyl substituted propanoic acid or derivative thereof; or,

(c) a combination of (a) and (b).

2. The composition according to claim 1 comprising: (i) one or more reaction products of the material and the graft monomer; or (ii) one or more products of the combination of the material and the graft monomer.

3. The composition according to claims 1 or 2 wherein the graft monomer is an unsaturated acid or anhydride or derivative thereof.

4. The composition according claims 1 or 2 wherein the graft monomer is maleic anhydride.

5. The composition according to claims 1-3 wherein the graft monomer before grafting has an olefinic bond through which it is grafted to the material.

6. The composition according to claim 5 wherein the olefinic bond is an α, β olefinic bond and the graft monomer is grafted to the material through the α, β olefinic bond.

7. The composition according to any of the preceding claims wherein the material contains less than 50% olefinic protons.

8. The composition according to any of the preceding claims wherein the material contains less than 5% olefinic protons.

9. The composition according to any of the preceding claims wherein the material contains less than 1% olefinic protons.

10. The composition according to any of the preceding claims wherein the oligomer is derived from a petroleum distillate boiling in the range of 30°C to 210°C.

11. The composition according to any of the preceding claims wherein the oligomer has a molecular weight between 130 and 500.

12. The composition according to any of the preceding claims wherein the oligomer is selected from the group consisting of oligomers of cyclopentadiene and substituted cyclopentadiene , oligomers of C_4-C_6 conjugated diolefins, oligomers of C_8-C_{10} aromatic olefins, and mixtures of two or more thereof.

13. The composition according to any of the preceding claims wherein the oligomer is derived from at least one aromatic monomer.

14. The composition according to any of the preceding claims wherein the grafted material has a softening point between 10°C and 200°C.

15. The composition according to any of the preceding claims wherein the grafted material has a softening point between 80°C and 150°C.

16. The composition according to any of the preceding claims wherein the grafted material has a softening point between 90°C and 110°C..

17. The composition according to any of the preceding claims wherein the grafted material has a Tg less than 120°C.

18. The composition according to any of the preceding claims wherein the grafted material has a Tg between 25°C and 100°C.

19. The composition according to any of the preceding claims wherein the grafted material has a Tg between 35°C and 70°C.

20. The composition according to any of the preceding claims comprising between 0.1 and 99 wt% grafted oligomers.

21. The composition according to any of the preceding claims comprising between 0.1 and 30 wt% grafted oligomers.

22. The composition according to any of the preceding claims wherein the oligomer:graft monomer mole ratio in the grafted oligomer is between 2:1 and 1:2.

23. The composition according to any of the preceding claims wherein the graft monomer:resin weight ratio in the grafted resin is between 1:100 and 1:2.

24. The composition according to any of the preceding claims further comprising at least one other resin selected from the group consisting of: aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic/aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic/aromatic hydrocarbon resins, aromatic hydrocarbon resins, at least partially hydrogenated aromatic hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosin esters, resins grafted with graft monomers, and mixtures of any two or more thereof.

26. The composition according to any of the preceding claims further comprising one or more oligomers of the graft monomer.

27. The composition according to any of the preceding claims further comprising at least one polyolefin.

28. The composition according to claim 19 wherein the polyolefin is selected from the group consisting of: polyethylene, an ethylene α-olefin (C_3-C_{20}) copolymer, polypropylene, a propylene α-olefin (C_4-C_{20}) copolymer, polybutylene, a butylene α-olefin (C_5-C_{20}) copolymer, a polyisobutylene polymer, α-olefin diene copolymers, block copolymers comprising styrene and a conjugated diene, and mixtures of two or more thereof.

29. The composition according to any of the preceding claims further comprising at least one polar polymer.

30. The composition according to claim 21 wherein the polar polymer is selected from the group consisting of polyesters, polyamides, polyureas, polycarbonates, polyacrylonitriles, polyacrylates, polymethylacrylates, ethylene vinyl acetate copolymers, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate, polyacetals, ethylmethyl acrylate, ethylbutyl acrylate, and mixtures of two or more thereof.

31. The composition according to any of the preceding claims further comprising a polymer comprising ethylene or propylene and having a CDBI greater than 50% and a polydispersity of less than 4.

32. The composition according to any of the preceding claims further comprising at least one wax or oil.

33. The composition according to any of the preceding claims further comprising at least one cross-linking agent.

34. A process comprising contacting a graft monomer with an at least partially hydrogenated material, wherein the material comprises:

(a) a thermally polymerized aromatic-containing hydrocarbon resin;
(b) an oligomer, in which case, the oligomer after it has been grafted with the graft monomer:

(i) does not comprise norbornyl ester groups; or
(ii) comprises at least one of a mono-alkyl succinic acid, anhydride or derivative thereof, or a β-alkyl substituted propanoic acid or derivative thereof; or,

(c) a combination of (a) and (b).

35. The process according to claim 34 wherein the graft monomer is an unsaturated acid or anhydride or derivative thereof.

36. The process according to claim 34 wherein the graft monomer is maleic anhydride.

37. The process according to any of claims 34-36 wherein the graft monomer before grafting has an olefinic bond through which it is grafted to the material.

38. The process according to claim 37 wherein the olefinic bond is an α, β olefinic bond and the graft monomer is grafted to the material through the α, β olefinic bond.

39. The process according to claims 34-38 wherein the weight ratio of graft monomer to material in the reaction mixture is less than 5:10.

40. The process according to any of claims 34-39 wherein the material contain less than 50% olefinic protons.

41. The process according to any of claims 34-39 wherein the material contain less than 5% olefinic protons.

42. The process according to any of claims 34-39 wherein the material contain less than 1% olefinic protons.

43. The process according to any of claims 34-42 wherein the oligomer is derived from a petroleum distillate boiling in the range of 30°C to 210°C.

44. The process according to any of claims 34-43 wherein the oligomer has a molecular weight between 130 and 500.

45. The process according to any of claims 34-44 wherein the oligomer is selected from the group consisting of oligomers of cyclopentadiene and substituted cyclopentadiene, oligomers of C_4-C_6 conjugated diolefins, oligomers of C_8-C_{10} aromatic olefins, and combinations of two or more thereof.

46. The process according to any of claims 34-45 wherein the oligomer comprises at least one aromatic monomer.

47. The process according to any of claims 34-46 wherein the graft monomer contacts the material in the presence of a free radical initiator.

48. The process according to claim 47 wherein the free radical initiator is selected from the group consisting of: benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(peroxy-benzoate)hexyne-3, 1,4-bis(tert-butylperoxyisopropyl)benzene, lauroyl peroxide, tert-butyl peracetate, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, tert-butyl perbenzoate, tert-butylperphenyl acetate, tert-butyl perisobutyrate, tert-butyl per-sec-octoate, tert-butyl perpivalate, cumyl per-pivalate and tert-butyl perdiethylacetate, azoisobutyronitrile, dimethyl azoisobutyrate, and mixtures of two or more thereof.

49. The process according to claims 47 or 48 wherein weight ratio of radical initiator to graft monomer in the reaction mixture is less than 5:10.

50. The process according to any of claims 34-49 comprising contacting the material with the graft monomer in the presence of a solvent.

51. A process comprising combining at least one other resin with a product produced by the process of any of claims 34-50.

52. The process according to claim 51 wherein the resin selected from the group consisting of: aliphatic hydrocarbon resins, at least partially hydrogenated aliphatic hydrocarbon resins, aliphatic/aromatic hydrocarbon resins, at least partially hydrogenated aliphatic aromatic hydrocarbon resins, cycloaliphatic hydrocarbon resins, at least partially hydrogenated cycloaliphatic resins, cycloaliphatic/aromatic hydrocarbon resins, cycloaliphatic/aromatic at least partially hydrogenated hydrocarbon resins, polyterpene resins, terpene-phenol resins, rosin esters, grafted resins, and mixtures of two or more thereof.

53. A process comprising mixing at least one polyolefin to a product produced by the process any of claims 34-52.

54. The process according to claim 53 wherein the polyolefin is selected from the group consisting of: polyethylene, an ethylene α-olefin (C_3-C_{20}) copolymer, polypropylene, a propylene α-olefin (C_4-C_{20}) copolymer, polybutylene, a butylene α-olefin (C_5-C_{20}) copolymer, α-olefin diene copolymers, a block copolymer comprising styrene and a conjugated diene, and mixtures of two or more thereof.

55. The process according to claim 53 wherein the polyolefin is a polymer comprising ethylene or propylene and having a CDBI greater than 50% and a polydispersity of less than 4.

56. The process according to claim 53 wherein the polyolefin is a polar polymer.

57. The process according to claim 56 wherein the polar polymer is selected from the group consisting of polyesters, polyamides, polyureas, polycarbonates, polyacrylonitriles, polyacrylates, polymethylacrylates, ethylene vinyl acetate copolymers, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate, polyacetals, ethylmethyl acrylate, ethylbutyl acrylate and mixtures of two or more thereof.

58. The process according to any of claims 34-57 further comprising admixing at least one wax or oil.

59. The process according to any of claims 34-58 further comprising cross-linking the resin material with itself or a polymer combined with the resin material.

60. A product produced by any of claims 34-59.

61. The use of an adhesive material comprising a product produced by any one of claims 26-49.

62. An article comprising a substrate selected from the group of: polyethylene terephthalate, paper, recycled paper, a film comprising one or more polyolefins, cardboard, recycled cardboard, substrates having acrylic varnishes thereon, wood, glass, ceramic, asphalt, concrete, and metal, the substrate having an adhesive composition adhered thereto, the adhesive composition comprising a composition according to any of claims 1-33.

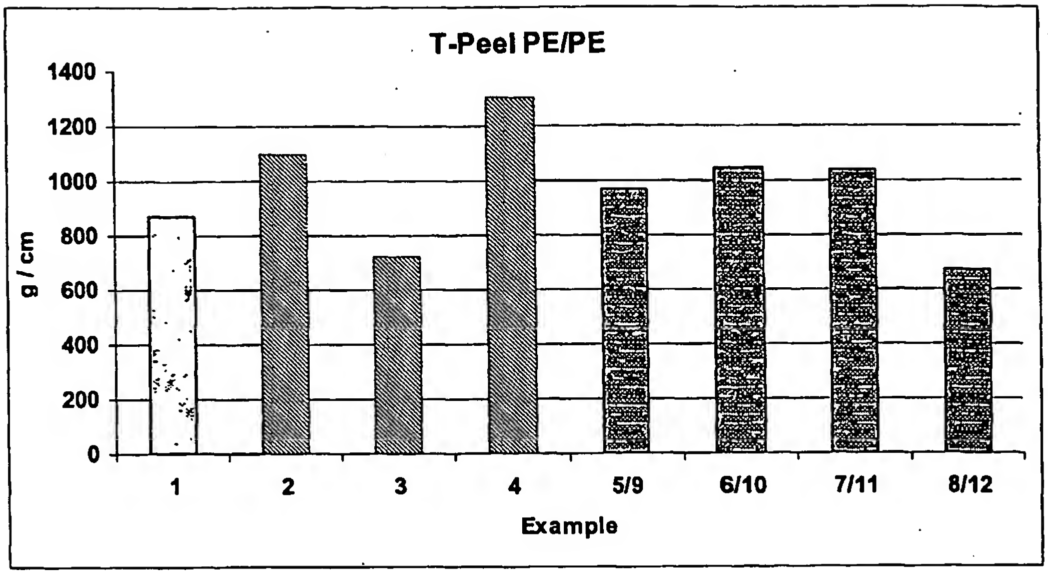

Figure 1

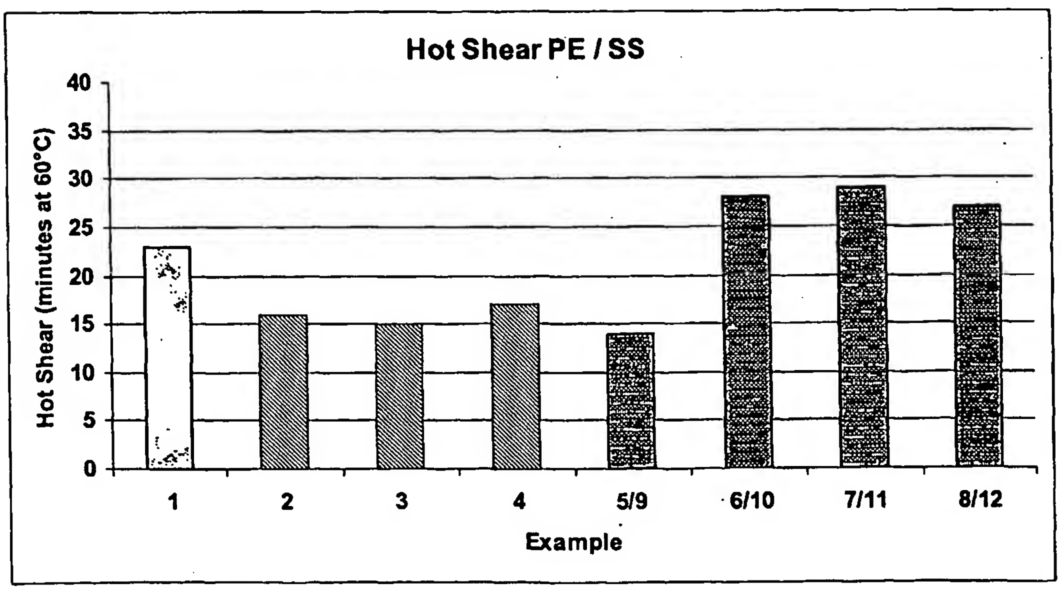

Figure 2

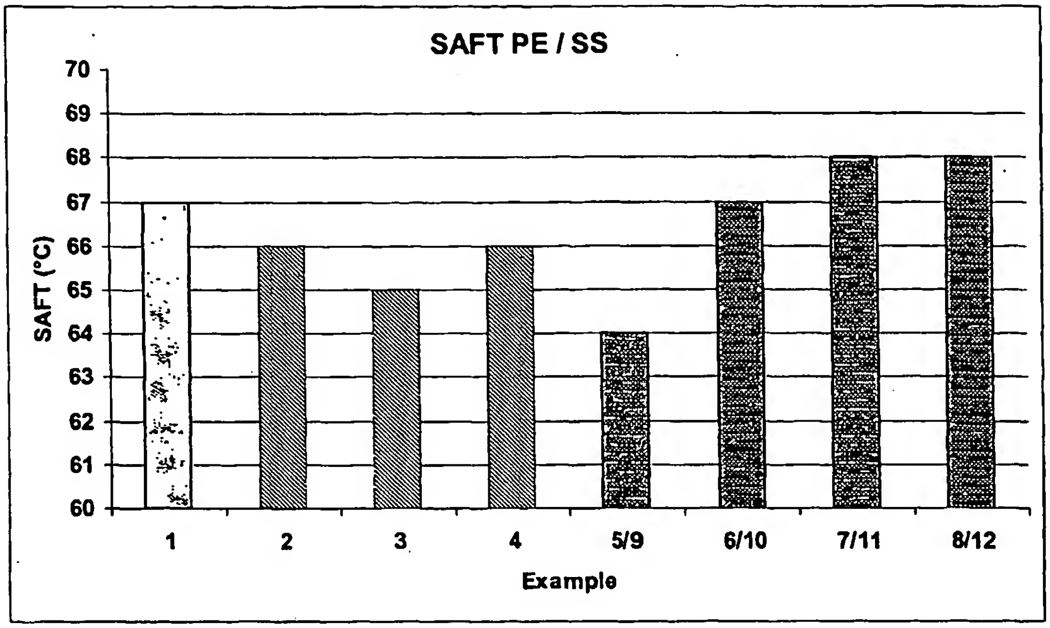

Figure 3

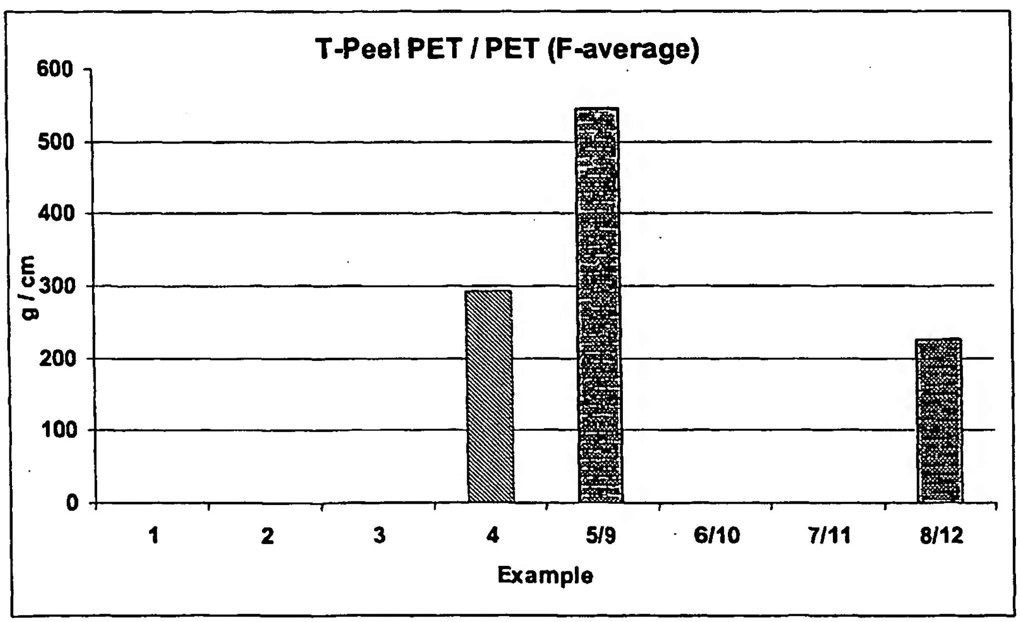

Figure 4

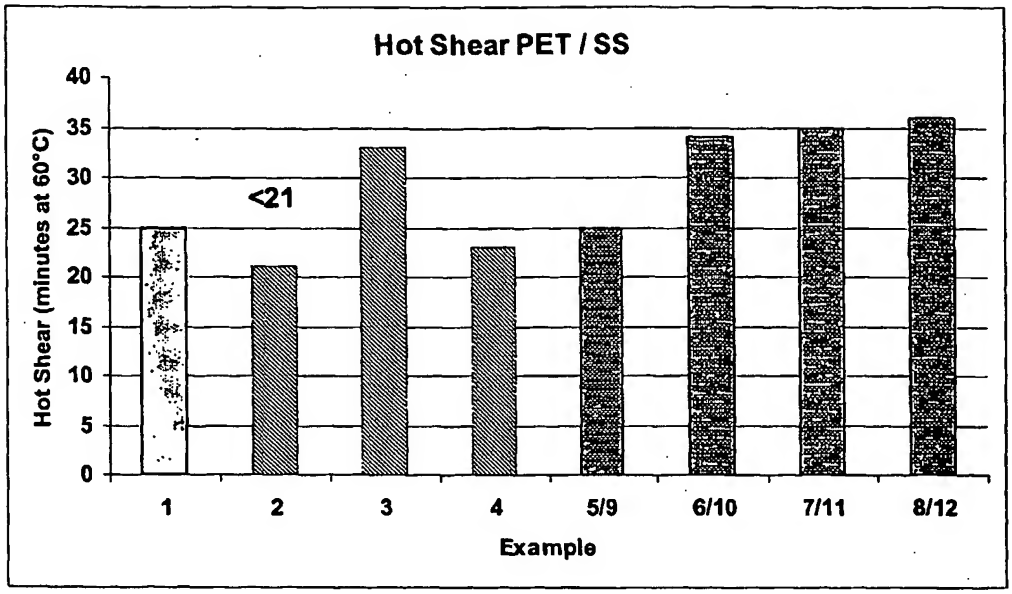

Figure 5

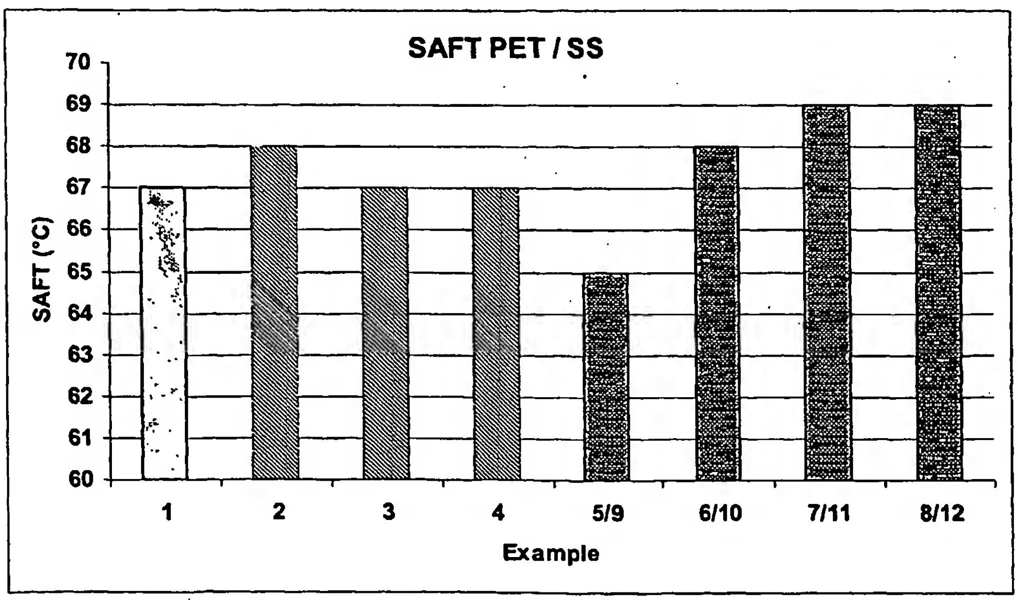

Figure 6

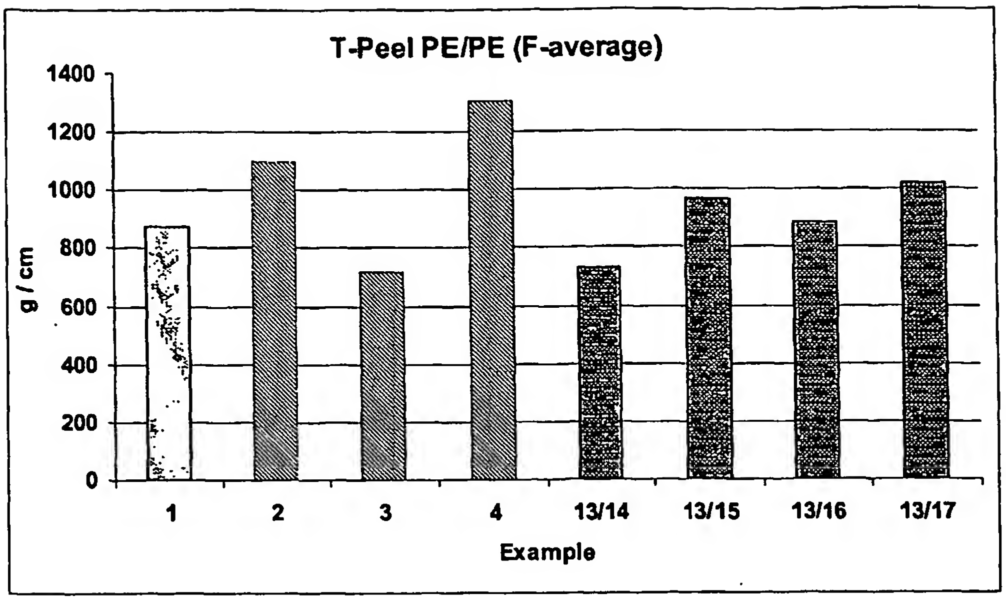

Figure 7

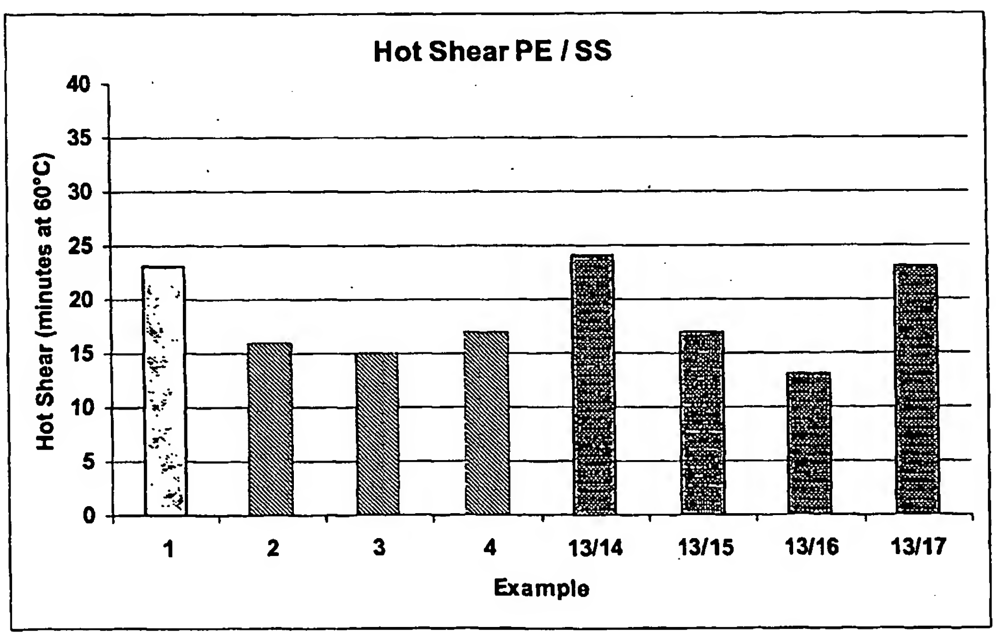

Figure 8

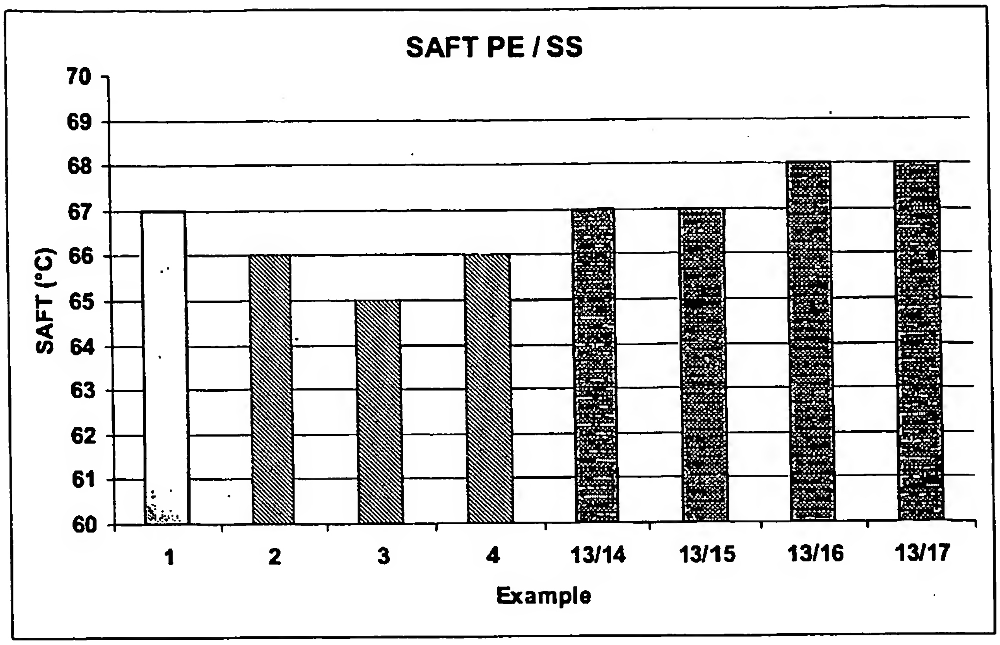

Figure 9

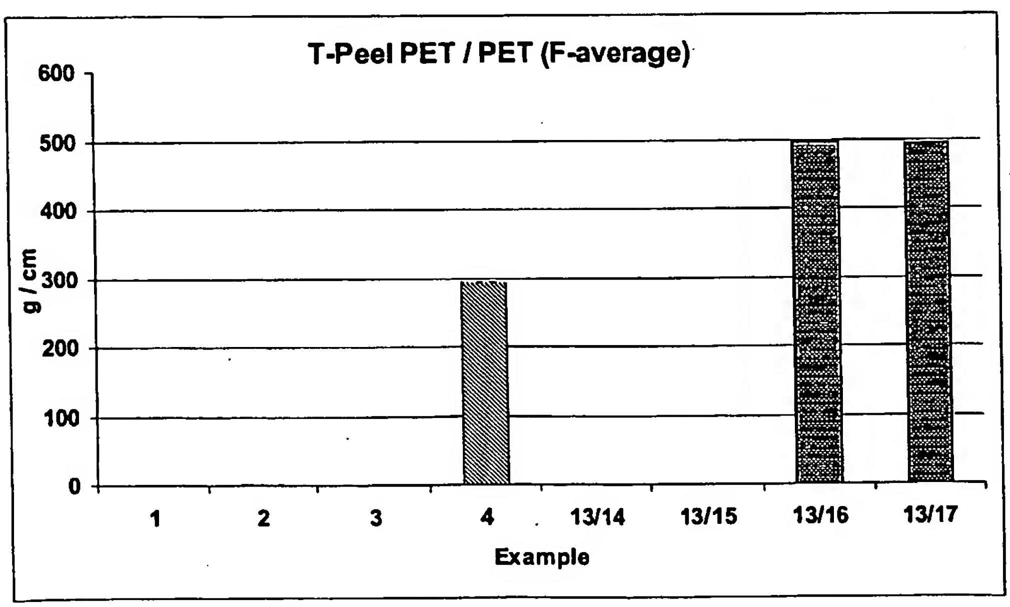

Figure 10

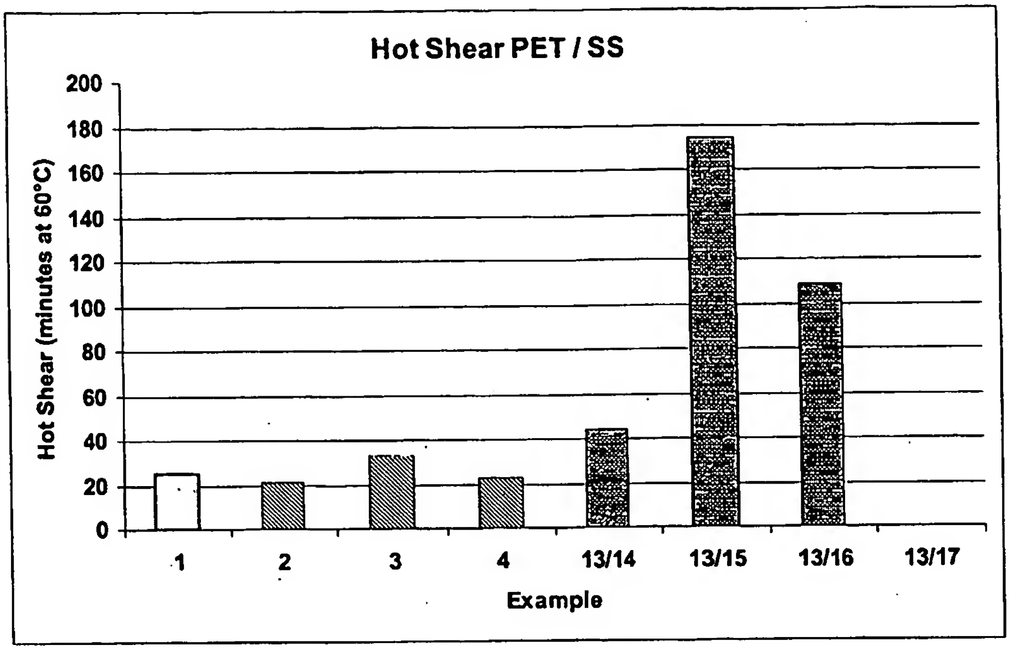

Figure 11

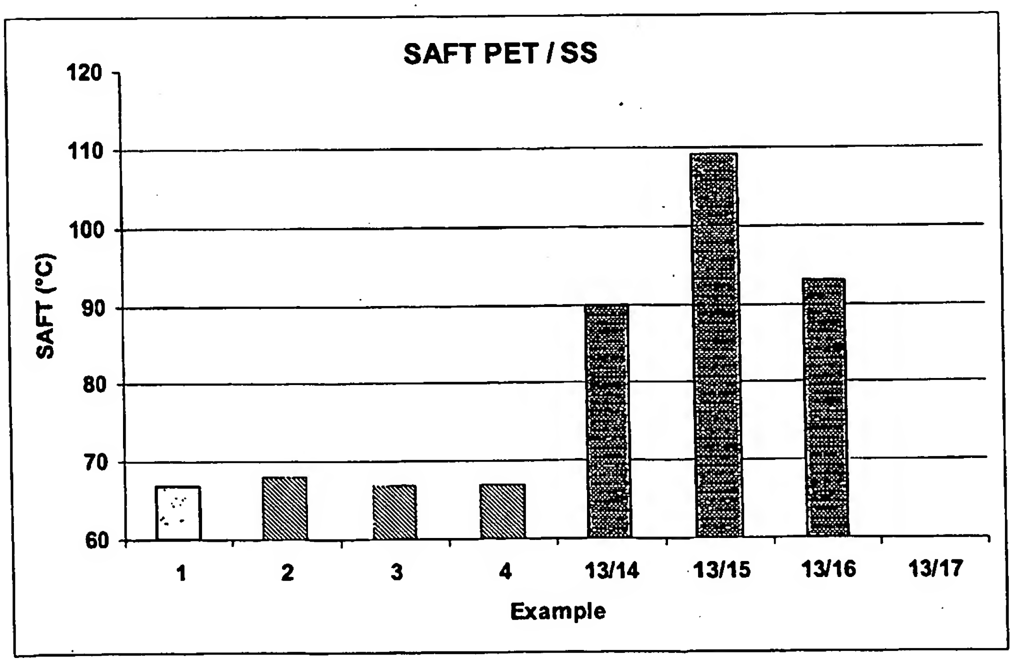

Figure 12

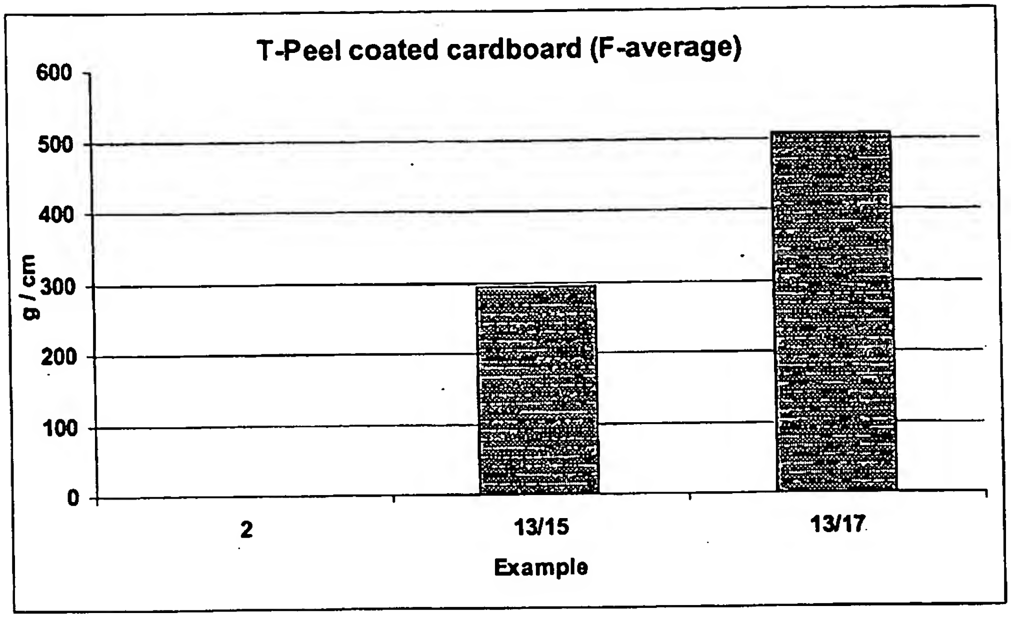

Figure 13

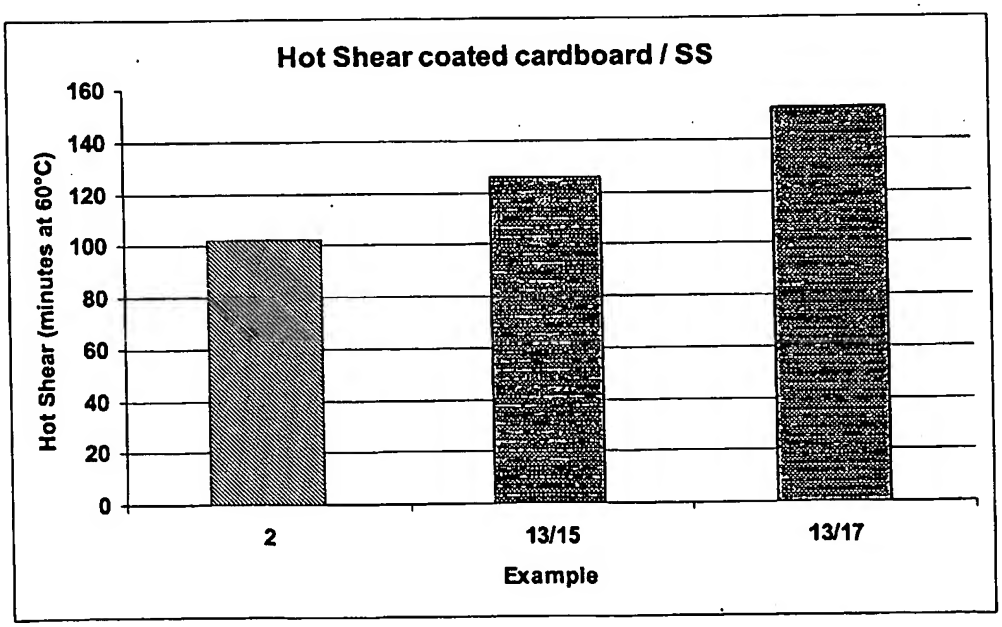

Figure 14

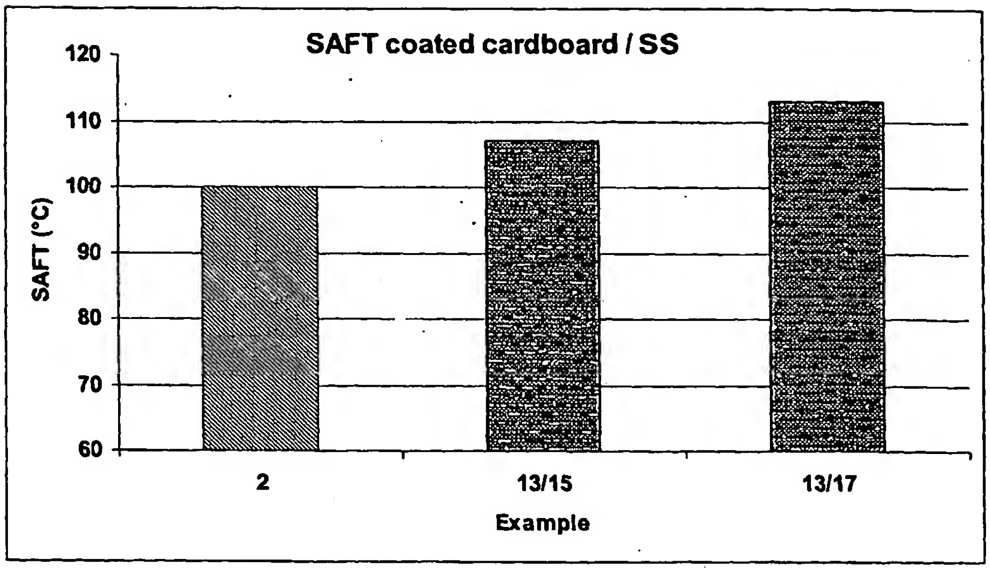
SAFT coated cardboard / SS
120
110
100
90
80
70
60
SAFT (°C)
2
13/15
13/17
Example

Figure 15

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 20 3566

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 90 15111 A (EXXON CHEMICAL PATENTS INC) 13 December 1990 (1990-12-13) * page 5, line 17-23 * * page 6, line 15-23; claims 1-6,10,11 *	1-23, 34-52	C09J151/00 C08F8/46 C08F289/00 C08F255/00
A	US 4 315 863 A (TOMOSHIGE TORU ET AL) 16 February 1982 (1982-02-16) * claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 March 2002	Meulemans, R

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 20 3566

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The members are as contained in the European Patent Office EDP file on
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06-03-2002

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82